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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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TITLE OF THE INVENTION (500 characters max)

THERMOFORMED FOAMED THERMOPLASTIC PACKAGING

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ENCLOSED APPLICATION PARTS ***(check all that apply)***

☑ Specification *Number of Pages* 31

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☐ Application Data Sheet. See 37 CFR 1.76

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Respectfully submitted,

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Branch et al.
Filed	:	5/17/2003
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Docket No. : MGP 03-01P

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- Postcard
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- Specification (31 pages)
- 6 Sheets of Drawings (Figures 1-12)

THERMOFORMED FOAMED THERMOPLASTIC PACKAGING

FIELD OF THE INVENTION

The present invention relates to packaging and methods for making and recycling packaging, and more particularly to food packaging and methods for making and recycling food packaging formed at least partially by thermoforming foamed thermoplastic materials.

BACKGROUND OF THE INVENTION

Plastic packaging accounts for a significant proportion of the US plastic market. While paper food packaging costs considerably more than conventional plastic foam, it enjoys a market lead due to environmental and health concerns regarding traditional polystyrene foam. In some applications, even at still higher costs, solid polyethylene terepthalate (PET) plastic is the preferred food package due to its advantages such as improved flavor retention, moisture barrier, and recyclability.

Despite conventional foams' benefits, they suffer a negative image in the perception of many consumers because of the environmental damage related to their manufacturing and disposal. Most foam has been produced using either HCFC fluorocarbons or explosive and noxious hydrocarbon fuel gases such as heptanes. Since HCFC grade 141b was banned in January 2003, some foam companies have switched to more expensive HFC fluorocarbons. HFC fluorocarbons still destroy ozone and add roughly 12% more material cost than hydrocarbons. There is a public perception that paper packaging, even though significantly more expensive than foam, is better for the environment. Paper

requires one or more layers of plastic to be a satisfactory prepared food-contact package, which then renders it practically non-recyclable. Even though 100% recyclable, solid PET plastic is expensive to use. Recyclable foamed PET packages, if economically manufactured, are an ideal solution.

In addition to posing environmental risks, conventional thermoplastic foams may pose health risks. Conventional polystyrene (PS) foam is made from a styrene monomer that is known to migrate from PS packaging into food and then into human tissue. The EPA National Human Adipose Tissue Survey for 1986 identified styrene residues in 100% of all samples of human fat tissue taken in 1982 in the US. Residuals from hydrocarbon gasses used during manufacture stay in the foam for months. Many consumers taste the residual hydrocarbon gases in coffee served in PS foam cups.

PS foam is typically of low density 5% – 15% solid when used for food packaging, insulation, and shipping containers. PS foam is generally made in one of two processes: (1) Expanded beads compressed together in a closed mold or (2) Conventional process.

In conventional foaming processes, chemical or physical blowing agents are used to create bubbles in liquid plastic concurrently with shaping the plastic product during an extrusion or injection molding process. Hydrocarbon fuel gases such as butanes, pentanes, and heptanes are widely used as blowing agents in conventional plastic foam production.

Certain other plastic materials are generally safe. An example is PET, which is the plastic used for soda-pop bottles. PET was designed for recycling. Pet has “no known risks” as a food-packaging polymer. Currently PET is not widely used in disposable food packaging for two reasons: 1) Solid PET is expensive compared to paper or conventional foam. 2) PET cannot be commercially foamed with conventional techniques.

The large amount of plastics in landfills is a widely recognized problem. Volume, degradability, and hazards of waste are primary concerns in the waste

stream. Major fast food chains and other organizations have made a concentrated effort to reduce the volume of the waste. Environmental organizations voice concerns over the non-decomposition of plastics, plastic foams, and paper. Recycling solves these problems.

Unfortunately, a lack of a viable foaming technology has prevented recycled PET from being used in low cost food packaging. One reason for this is that he variability of recycled polymer makes it extremely difficult to conventionally foam any plastic with recycled content. A process that allows foaming recycled PET economically will significantly reduce plastic waste in landfills.

For years, customers and food vendors searched for a disposable coffee cup that was not too hot to hold, would keep the coffee warm, and did not contaminate the coffee or our planet. Even though they appreciated their insulating quality, consumers rejected PS foam cups as too polluting and unhealthy. Major coffee vendors have used an additional costly insulating sleeve to satisfy their customers. Many food-packaging products call for the insulating qualities of foam without the hazards of PS foam.

Thermoforming is a conventional method for forming 3 dimensional shapes from flat polymer sheets. The process heat softens the flat polymer sheet and then vacuum or pressure forms the sheet onto a die with the required shape. Thermoforming produces general packaging as well as PS Foam Clamshells and solid plastic cups. When thermoforming is used to form a deep product such as a coffee cup, etc. from a flat plastic or foamed sheet, it is termed a deep draw.

U.S. Patent No. 4,473,665 is directed to a two-stage method for foaming thermoplastics. That patent describes a first stage wherein a polymer is placed in a pressure vessel for saturation with high-pressure gas. During a second stage, the polymer is heated to the Tg at a much-reduced pressure. The gas, previously forced into the polymer at high-pressure, foams the polymer when the polymer temperature reaches a temperature that sufficiently softens the plastic.

U.S. Patent No. 5,684,055 is directed to a method for foaming a long strip or roll of polymer whose length may be greater than the pressure vessel's greatest interior dimension. In a first stage, a roll of flat polymer stock with porous separator material between each roll layer (alternately a group of sheets with a separator between each sheet) is placed into a pressure vessel for saturation. The second stage involves unrolling the polymer, heating it to the required foaming temperature, and quenching it to stop the foaming process as desired.

U.S. Patent Nos. 5,223,545 and 5,182,307 are directed to a process and product made in a manner similar to the saturation process described in the above patents, but specifying the use of carbon dioxide gas (CO_2) with PET polymer.

While advances have been made in the field of thermoformed-foamed polymers, there remains a need for improved products and methods related to the manufacture of such products.

OVERVIEW OF THE INVENTION

In various aspects, the present invention relates to foamed thermoplastic materials, methods and apparatus for foaming thermoplastic materials, methods and apparatus for thermoforming foamed thermoplastic materials into packaging, structures, and the like, packaging formed from thermoformed foam thermoplastic materials, as well as to methods relating to use including recycling of foamed thermoplastic materials and trim from the manufacture thereof.

In some aspects, the invention relates to use of a microcellular foam technology for packaging that generally offers higher performance than alternatives; including significantly more insulation than coated paper packages of the same size, a healthy package that eliminates migration of chemicals into food, relatively high strength, leak, and cut resistance compared to alternatives, and dual

ovenability – packaging that can be used to reheat food in a conventional oven or in a microwave oven.

In another aspect, the present invention teaches an ability to foam 100% recycled content PET and other polymers.

In another aspect, the foaming process taught herein avoids the use of noxious gases such as pentane and heptane. Thus, residual gases will not contaminate food and manufacturing process safety may be improved due to eradication of explosive gases.

In another aspect, the manufacturing process avoids the use of ozone depleting gasses such as HFCs, HCFCs, etc that are steadily being outlawed worldwide.

In still another aspect, the manufacturing process may form an integral skin, such as a smooth skin of PET for instance. The integral skin has substantially the same chemistry as the walls of the gas cells enclosed thereby. The integral skin may act to improve rigidity, abrasion resistance, imperviousness to stains and liquid ingress, appearance, and other desirable qualities. The integral skin may increase strength, increase package sanitation, and give packages the look and feel of solid plastic.

In another aspect, the process forms plastic foams that are characterized by micro-cells within the foam. A micro-cell's diameter may be so small as to not be visible to the unaided human eye. The plastic foam may appear to be solid, even in cross-section.

In another aspect, a method is provided for thermoforming foam semicrystalline-polymers with control of the unfoamed skin thickness, independent control of the depth and percentage crystallinity of the surface layers, as well as the core percent crystallinity. This method also reduces energy consumption, increases quality, and significantly increases production rate of thermoformed polymer foams. This method uses high levels of gas-induced crystallinity prior to thermoforming and results in higher allowable service

temperature limits. The reversible plastizing imbued upon the thermoplastic by the foaming gas increases the allowable depth of draw during thermoforming.

In another aspect, a thermoformed semicrystalline-polymer material is taught, the material having an unfoamed skin of controllable thickness and percentage crystallinity as well as a foamed core with a lower percent crystallinity. The "gas-impregnated thermoformed" material allows higher formed part service temperatures than conventional through crystallized solid PET thermoformed parts with similar impact strength. Alternately, "gas-impregnated thermoformed" polymer allows higher formed part impact strength and ductility than conventional through crystallized solid PET thermoformed parts with similar maximum service temperature. Further, this material increases the practical depth of draw or the maximum practical crystallinity level for a given depth of draw during a thermoforming operation. Other semi-crystalline polymers experience similar benefits when thermoformed after being injected with crystallizing gas.

Another aspect is directed toward increasing formability and saving energy during thermoforming of all polymers, whether semi-crystalline or amorphous, and whether cellular foams or solid.

In still another aspect, a food-to-go container is fabricated from foamed thermoplastic, such as PET for example. The container, which may be used for consumer, food processors, and institutional applications, includes features for maintaining desirable properties of food such as freshness, crispness, crunchiness, heat, cold, etc. Additionally, the material may be formed to withstand relatively large swings in temperature including, for example, freezer-to-oven, refrigerator-to-microwave, etc. This allows consumers and institutions to use the packaging for processing, cooking, storage, reheating, serving, etc.

In another aspect, methods are taught for making foamed packaging, structures, and the like from a thermoplastic sheet material that has a gas dissolved therein.

In yet another aspect, a foamed material, which may be formed into containers and the like, is substantially 100% recyclable.

In another aspect, structures may be formed of a foamed thermoplastic material. For example, walls or enclosures for inexpensive consumer products or other products that may be, for example, high volume, disposable, or cost sensitive may be formed by pressure or vacuum molding a thermoplastic sheet that has gas dissolved therein. Upon raising the material to or near to its glass transition temperature, the dissolved gas expands and improves the insulation, rigidity, and other aspects of the material, making it suitable for such walls or enclosures.

In another aspect a method is taught for selectively making portions of a plastic material opaque through the selective formation of air bubbles therein. By applying heat to a portion of a thermoplastic having a gas dissolved therein, the gas expands in those areas, causing the plastic to become more opaque or less transparent.

In another aspect, a container includes an indicator for indicating it has been heat cycled. Heat cycling of a thermoplastic material having gas dissolved therein causes the plastic to become more opaque or less transparent. Thus, relatively transparent containers formed from such plastic have not been heat cycled. Relatively opaque containers formed from such plastic have been heat cycled.

In still another aspect, an object may be formed of a foamed or nascently foamed thermoplastic material combined with an unfoamed thermoplastic material, the foamed or nascently foamed and unfoamed portions thereof having substantially equivalent chemistries. The portions may be joined, for example by thermal or solvent welding, or alternatively may be formed integrally.

In another aspect, a foamed thermoplastic food or drink container contains no solvent residues or other undesirable chemical reactivity that can spoil the taste or quality of the food.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a process for making, using, and recycling packaging.

Figure 2 is a cross-sectional view of a foamed thermoplastic having an integral skin.

Figure 3 is an isometric view of a food package having features for ease-of-use and for maintaining food quality.

Figure 4 is a cross sectional view of the food package of Figure 3.

Figure 5 is an isometric view of a rectangular food package.

Figure 6 is an isometric view of another food package.

Figure 7 is a block diagram showing details of consumer use of a food package made according to the present invention.

Figure 8 is schematic representation of a method for foaming and thermoforming a thermoplastic polymer sheet material showing additional detail of the converting operation compared to Figure 1.

Figures 9 and 10 are cross-sections of polymer structures obtained before and after thermoforming when used with high levels of gas-induced crystallinity prior to thermoforming.

Figures 11 and 12 are cross-sections of polymer structures obtained before and after thermoforming when used with low levels of gas-induced crystallinity prior to thermoforming.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned above, this invention is generally directed to improved thermoformed polymers, as well as to improved methods related to the

manufacture thereof, improved packaging and methods of making packaging therefrom, and use including recycling thereof.

Figure 1 is a block diagram of a process for making, using, and recycling packaging according to the present invention. A thermoplastic resin is manufactured 102 and extruded into sheets 104. Although in principle many thermoplastic sheet materials may be converted into foamed containers according to the present invention, PET and partially crystalline PET (C-PET) are preferred for many of the containers and especially food containers described herein because those materials are especially desirable for, and recognized by the FDA for direct food contact. A desirable property of the process described herein is that the foaming agents reversibly plasticize the thermoplastic, enabling the use of C-PET throughout the process rather than requiring it to be formed in situ during finishing. In another aspect, the process allows higher degrees of crystallinity in the finished product, a property that generally increases hardness and thermal stability of the finished product. In another aspect, the process allows variable crystallinity through the section of products formed therefrom, thus enabling customization of material properties.

Often, sheet extrusion takes place at an extrusion facility 105 which may or may not be separate from the resin manufacturer 103 and the conversion facility 106. In many cases, recycled resin is combined with virgin resin to make the extruded sheets. The FDA allows 100% recycled material with up to 58% post-consumer recycled material to be used for food contact. Heretofore, there have not been processes for foaming PET or C-PET that have not resulted in chemical alteration of the material, thus removing the possibility of recycling such foam materials. In contrast, one aspect of the present invention is that substantially all changes induced in the material, including crystallization thereof, are reversible, thus preserving recycleability. In the extrusion step 104, rolls of solid PET may be made, for example, from recycled soda bottles, recycled foamed PET made

according to the present process, and post-consumer recycled PET including recycled PET and C-PET foam made according to the present invention.

When the conversion facility 106 receives the thermoplastic sheets, the sheets are preprocessed 108 to make them ready for fluid saturation. Often, preprocessing involves interleaving a fluid permeable material with the extruded sheet and re-rolling the two materials into lengths that can fit into a saturation vessel. Before, during and after preprocessing, waste material may be gathered for recycling 118.

After preprocessing, the material is substantially saturated with a working fluid 110. The material is saturated by exposing it to a gaseous working fluid under pressure. For example, PET or C-PET may be exposed to carbon dioxide at 250 to 2500 PSIG, and especially approximately 270 to 2430 PSIG. The high pressure causes carbon dioxide gas to soak into the plastic rolls. Once saturated with gas the plastic roll is removed from the pressure vessel and proceeds to step two of the process. With the working fluid thus forced into the polymer matrix, the material may be thought of as nascent foam. Because the working fluid, in preferred embodiments, does not react chemically with the thermoplastic material, the material is not chemically altered and thus may continue to be recycled. The working fluid does, however, reversibly plasticize the material, reducing its glass transition temperature, T_g, and making materials with normally high T_g more amenable to processing.

After saturation and before expansion, the material may be held for a quiescent period of time 111. When held at a pressure and/or temperature lower than the pressure and temperature of the saturation step such as ambient temperature and atmospheric pressure for instance, the material is, in fact, supersaturated. During the quiescent period, which may be adjusted and may be accompanied by environmental changes such as pressure changes, temperature changes, etc. according to desired properties of the material, dissolved working fluid at the surfaces of the sheet escapes into the surrounding environment. In the

case of a carbon dioxide working fluid, it is permissible to allow the escaped gas into the atmosphere or alternatively to be recycled. By allowing the surface working fluid to escape, the localized material at the surface is no longer a nascent foam and will not form a foam during subsequent processing. The thickness of the surface layer thus affected may be adjusted by adjusting the quiescent time or otherwise changing the environmental conditions. Longer times allow more gas to escape, resulting in thicker surface layers. The surface layers are useful for improving cosmetic appearance and for enhancing abrasion and cut resistance. Generally the quiescent period may last from 10-24 hours for example. Refrigeration of the material during the quiescent or "de-sorption" period can extend it for greater process flexibility.

The nascent foam is then expanded into a closed microcellular foam by expanding in the presence of heat during expansion 112. The gas-saturated plastic roll is unwound and as it is been unwound it is fed into a heating tunnel in which it is heated. The heat causes the plastic to soften and the absorbed gas in the plastic coalesces into billions of small bubbles. The plastic expands in volume while retaining a surface skin of unfoamed plastic. At the exit end of the tunnel the resulting foam looks completely solid and still is a flat sheet. When heated to near its T_g the polymer matrix relaxes, thus allowing the high pressure dissolved working fluid to expand at the reduced pressure of the expansion apparatus. For PET, which has a T_g of approximately 150° C, this may be done in a hot air tunnel, by surface contact, by radiation heat transfer under infrared emitters, in hot liquid, or using other methods known to the art.

Expansion of the foam forms a structure shown in Figure 2 and/or Figures 9 or 11.

After, or coincidental with expansion 112, the thermoplastic sheet is finished by altering it into the form desired by the application. For the foam packages described herein, finishing may comprise die cutting and thermoforming for example. The flat foam sheet is then fed into the finishing stage 114. In the

finishing stage, the foam sheet may be fed into a standard forming machine called thermoformer, which heats and forms the flat sheet into three dimensional shapes such as cups, clamshells, trays, etc.

After delivery of the finished product through the delivery chain, the package is delivered to the consumer. The foam may subsequently be reclaimed and recycled back into the process. Because of the lack of chemical alteration of the material according to the present foaming process and because of the lack of contamination with trace solvents etc, the foam is recyclable.

Some notable aspects of this process include:

1. Ability to foam material whose melt viscosity has not been increased from the base material (and thus eliminating the need for undesirable additives and irreversible chemical processes),
2. Ability to foam material that has not been cross-linked (a method commonly used in increase viscosity in conventional foaming processes),
3. Foaming in the solid state where the material is never fully melted (thus preserving micro structures such regions of crystallinity and micro-bubbles), and
4. Foam that comprises micro-bubbles of uniform size and distribution.

Compared to conventional processes, which foam in the liquid state and struggle to control the size and distribution of bubbles by altering, sometimes significantly, the chemistry of the material, the present process operates on native materials that are not irreversibly altered. This non-alteration of the base material yields a material substantially identical to the base material in chemical structure and which is especially amenable to recycling.

Figure 2 is a cross-sectional view of a foamed thermoplastic having an integral skin. The process of Figure 1 may create a package having the cross section of Figure 2. The material at the center of the sheet 202 may be foamed at a ratio of about 10% to 99.9% solids, for example. In general, the foam is of a

microcellular, closed cell type. Surfaces 204a and 204b, which may be substantially identical to one another, are solid skins having substantially identical chemistry as the foam core 202 or at least being reversibly altered from the core material and from the original sheet material. Similarly, the core materials is reversibly altered from the original material via physical changes.

In some embodiments, the cross section of Figure 2 is formed of polyethylene terepthalate (PET) or semi-crystalline polyethylene terepthalate (C-PET). PET and C-PET have advantageous food contact properties, releasing neither un-scrubbed monomers such as styrene monomers, nor residual solvents into the food. Solid, non-foamed skins 204 possess enhanced appearance, sanitation, and cut and abrasion resistance compared to the foam surfaces of competing foaming processes. In another embodiment polybutyl terepthalate may be used for this and other containers described herein.

The thickness of skins 204 can be controlled by modulating degassing 111, greater thickness achieved by allowing additional degassing time, maintaining a warmer but sub-glass transition temperature environment, maintaining lower ambient pressure, reducing the thickness of the gas boundary layer, or a combination thereof. In a preferred embodiment, each skin 204 is 3% to 25% the total cross sectional thickness. In addition to other advantages, the process described herein creates skins on the foam that are much tougher than skins produced with extruded or molded foams which are not integral to the foam.

Figure 3 is an isometric view of a food package 301 formed by the process described herein. Figure 4 is a cross sectional view along section line 4-4'. The particular example of Figures 3 and 4 is a pizza container. Bottom 302 may optionally be joined to top 304 via a living hinge 306. Alternatively, the pieces may be formed separately. In a preferred embodiment, the bottom 302 or both top and bottom 304 and 302 of pizza container 301 is or are formed foam or partially foamed material fabricated according to processes described herein. Pizza container 301 may include one or more handles 308, here indicated as separate

handle halves 308a and 308b, to make it easier to handle the container when it contains hot pizza. Bumps, protrusions, or ridges 310, which may be embodied as other equivalent features, may be formed in the bottom of the container to keep the crust of the pizza substantially away from the bottom of the container. These features can help enhance the crispness of the pizza crust and also provide a place for excess oils to drain. Pizza container 301 may be formed as a round or ovoid shape or may alternatively be square or rectangular. The recycleability of the materials of the present invention may make a round container especially attractive owing to its improved aesthetics with concurrent elimination of concern about the waste produced during the manufacturing process.

The pizza box of Figures 3 and 4 may have an optional inner tray 402 that may act as a baking, cutting, and/or serving tray. The tray may be shaped to be substantially the same shape as the outer box, having one or more handles 404 to ease removal and handling. The outer box may be formed of a relatively low density foam while the inner tray is formed of a relatively high density foam having a higher crystallinity. To facilitate the cutting, the tray may be made at higher density or with a thicker unfoamed integral skin (as explained in patent 5,684,055.) than required for the box. Higher crystallinity of the inner tray imparts higher temperature stability and allows it to act as a baking sheet. The lower density outer box enhances thermal insulation during transport. In preferred embodiments, the foam has a relative density of 5 to 50% (for PET, 25% relative density is PET foam with a density of 33 gm/cc (0.25 x 1.31 gm/cc). In especially preferred embodiments, the box has a density in the 5-25% relative density range, while the tray's density range is 8-35% relative density. In preferred embodiments of the pizza box and allied applications, the crystallinity level of the PET foam is 19% - 35%.

Inner tray 402 may be held off the bottom of the outer box by bumps 310, for example, to further improve thermal isolation from the exterior. Alternatively, concave upward bumps may be formed in the tray itself or other features can be

added, such as drain holes to drain oils and grease away from the food into the bottom of the outer box. In a preferred embodiment the upper surface of inner tray 402 is relatively flat and smooth to facilitate cutting.

The pizza box 301 of Figures 3 and 4 may be delivered to or taken home by the consumer with a cold or a hot pizza contained therein. If hot, the high temperature resistance of C-PET makes it possible for the producer to cook the pizza right in the box, or right on the inner tray, or alternatively put the cooked food directly into the box without fear of melting it. The insulating characteristics of the foam material enhance maintenance of serving temperature. The cut resistance of the integral skins make the box attractive for cutting the pizza directly thereon. The superior aesthetics of the material make it advantageous to serve the pizza directly from the container. The cracking resistance and wide thermal stability of the material make it possible or desirable to refrigerate or freeze unconsumed leftovers directly in the box. The high thermal stability of C-PET makes it advantageous to reheat the pizza by microwave oven, convection oven, conventional oven, or other means directly in the box. Finally, the entire package may be recycled, owing to the integral nature of the skins with their inherent chemical similarity to the core foam, lack of flammable gases, and lack of chemical change to the polymer during or required by the foaming process.

The round shape of the pizza box of Figures 3 and 4 is advantageous with respect to heat retention. Insofar as heat retention is a function of surface area, a round pizza box has somewhat less than 80% the surface area of an equivalently dimensioned square box (78.54%). Therefore, a round pizza box will keep the pizza warmer longer.

The food container of Figures 3 and 4 is also amenable to other food applications such as a take-and-bake cookie box with integral cookie sheet or other brown-and-serve applications for example.

Because of the high temperature compatibility of C-PET, polybutyl terpthalate, and other materials that are not compatible with conventional foaming

processes, food containers formed by the process described herein, such food containers may eliminate typical warning labels such as “Do not microwave”, “Avoid high temperatures”, etc. typical of foam materials. This may be used to advantage in take-home fast food containers, such as chicken containers for example, in allowing the consumer to reheat the food directly in the container rather than requiring removal, as present warning labels on conventional foam containers advise.

Because of the substantially 100% recyclability of foam materials created according to the present process, round containers and other container shapes that normally would be prohibitive because of the relatively large amount of trim are especially feasible. This allows containers to be fabricated in shapes more optimized for the application, having properties such as improved aesthetics, improved heat retention, etc.

Figures 5 and 6 are isometric views of other embodiments of food containers 301. Figures 5 and 6 include a closure comprising slots 502 and tabs 504. The closures shown in Figures 5 and 6 or alternative but equivalent functionality features may and preferably are included in the pizza box 301 of Figures 3 and 4. The food container 301 of Figure 5 includes bottom 302 and top 304. Optionally, top 304 or a portion thereof may be left unfoamed, and therefore transparent to maximize aesthetic qualities. As described elsewhere, this is accomplished by not exposing that portion of the package to heat until after outgassing has been completed. Bottom 302 and optionally top 304 may be foamed to maximize rigidity and insulating qualities.

Figure 6 illustrates a circular food container 301. Such a shape is especially feasible with the present material technology because of the substantially 100% recyclability of the waste produced by die cutting. It is a preferred embodiment because its reduced surface area enhances thermal insulation qualities.

The containers of Figures 3 through 6 are indicative various aspects of a broad variety of applications. For example, many restaurants have take out boxes,

the majority of which are made from polystyrene foam. Customers are offered the boxes to take home the left over portions of their meal. The polystyrene foam box easily tears, and cannot be put in the oven or microwave to reheat. The takeaway box of thc present invention, when made from PET foam is durable, of superior insulation value to the polystyrene foam, and the food can be re heated in the oven or microwave without removing from the box. All or most of the steps necessary for preparation, storage, transport, and eating and storage of the "leftovers" of various kinds of food items can be accomplished without removing the food from the package.

Another application is reusable or semi-disposable PET foam food containers. Food today is quite often stored in plastic containers. Some are non-microwavable and few or none are ovenable in a conventional oven. PET foam containers made from FDA approved recycled PET can be used to store leftovers from meals to be re heated by microwave or oven. Some existing containers are thick and hcavy and intended to be reused for years but are high cost. Others are thin, solid, and intended to be used a few times or at most a few dozen times before they become cut, stained, and unsanitary but can be readily disposed of due to their low cost. Still other existing packages are foams intended to be used only once for orginal packaging and then transport but not for cooking, cutting, re-heating, etc. These foam packages are very low cost. The packages herein describcd are semi-disposable, but at a cost similar to the one use conventional foam packages. The packages described here can be sealed with a matching foam lid, solid plastic lid, or cling film for storage, can also be used for food storage in fridge or freezer and can be reused. A separate serving/cooking tray may be incorporated to fit inside the box and may be of a higher density and toughness than the outside box to optimize the inner tray for cutting.

Advantages of scmi-disposable packages of the present invention compared to existing heavier solid plastic containers, lighter thinner solid containers, or foamed plastic containers include:

1. Lower cost due to reduced material and the use of significant recycled material content.

2. Higher rigidity even with less material used due to increased wall thickness

3. Increased insulation to keep hot foods hot and cold foods cold longer for travel or "lunch box" use.

4. The food can be pre-cooked, frozen, cooked, transported, served, stored, reheated, stored, etc., all without using another container or package or serving plate due to the integral skin, use of high crystallinity PET foam, and the internal tray.

5. Use of 1- 100 % recycled plastic content used to create the PET foam saves costs and lowers the environmental cost of disposable packaging.

6. Greater service-temperature range due to the choice of PET or C-PET material.

7. Where advantageous, the use of a separate internal tray of higher density foam allows preparation, cooking, cutting, and serving without the sides of the container interfering with the access to the food and with enough strength to allow the above processing and eating steps. The outer container is of lower density to add insulation and reduce costs. The tray is located against sliding within the box by its handles and corresponding slots or notches in the box into which the handles snap.

Figure 7 is a block diagram illustrating use of the containers by the consumer. As indicated, containers described herein may be used for multiple functions, including initial delivery (with enhanced insulation of hot or cold foods), serving, storage (for instance in a refrigerator or freezer), reheating and subsequent use. Finally, because of the elimination or reduction in chemical alteration of the material during processes described herein (ignoring crystallinity changes, which do not change chemistry), the material may be recycled in its entirety.

Referring now to Figure 8, a roll of flat polymer stock with porous separator material between each roll layer (alternately a group of sheets with a separator between each sheet) is placed into a pressure vessel for saturation. The pressure vessel is filled with CO2 gas to allow the gas to saturate the polymer. The gas serves as a physical blowing agent. The gas also serves to lower the polymer Tg, the rigidity, and melting temperature. The saturation time in the pressure vessel is dependant upon pressure, the desired gas-to-solids ratio, the geometry of the roll, the thickness of the flat polymer stock, and other variables. For example, with CO_2 gas at 40 atmospheres pressure saturating PET at room temperature, a typical time in the pressure vessel is 190 hours. At this time the surface crystallinity may be above a 19% threshold that restricts later foaming. Saturation time longer than this increasingly creates a deeper crystallization layer and also increases the percentage of crystallization at a given depth. Saturation pressures may range from 20 to 180 atmospheres or more.

While this description is exemplified with PET, it should be recognized that other polymers or mixtures of polymers may be used in place of or in addition to PET. Suitable gas-polymer systems include CO_2 and Polypropylene, as disclosed in *CO_2-Assisted Crystallization of Polypropylene for Increased Melting Temperature and Crystallinity* by Mitsuko Takada et al, Proceedings of Polymer Processing Society meeting, Hertogenbosh, Netherland, May 31, 1999. Other gases and pressures may be used (for example, CO_2 may be used with polyethylene, polyvinyl chloride, acrylonitrile butadiene styrene, polycarbonate, polyethylene terephthalate, and polypropylene; and N_2 gas maybe used with polystyrene). In preferred embodiments, the gas acts to reduce the Tg or melt temperature of the polymer.

The gas impregnation of the polymer may take place either below or above the gas's supercritical pressure. Pressures as high as 180 atmospheres have been successfully used to foam polymers. Higher pressures result in a higher level of

gas impregnation with a maximum of about 30% by weight of gas dissolved in the polymer.

By controlling the saturation time, pressure, and temperature in the first stage, heavily crystallized PET surface layers are formed before foaming. The second stage of that process, subsequent foaming with heat, does not foam the heavily crystallized layers. Once the desired skin depth is crystallized above a threshold percentage level (about 19% for PET) the skin will not foam during the subsequent foaming operation. This limits the depth of crystallinity level that has obtained 19% or more, to a thickness less than or equal the desired finished unfoamed skin thickness. The "desorb time" or quiescent period (elapsed time after removal from the high pressure tank until heating for foaming) may also control the depth of the unfoamed surface skin.

The term "skin" refers to the integral unfoamed polymer produced by the semi-continuous process without regard to the crystallinity levels. After foaming, a layered structure exists that includes two surface layers consisting of highly crystallized PET and an interior at a lower crystallinity level as illustrated in Figures 9 through 12. Immediately after foaming, the thickness of the surface unfoamed skins may be greater than the raised crystallinity level layer as illustrated in Figure 9, Case A, or may be approximately equal in thickness, as illustrated by Figure 9, Case B. This previously foamed sheet or roll stock may then be thermoformed in a conventional thermoformer during which all layers may have their crystallinity levels raised, as illustrated by Figure 10, Cases A and B.

Crystallization also takes place during thermoforming heating and stretching operations depending on time, temperature and stress levels. Thermoforming crystallization takes place throughout the material thickness approximately uniformly. The biaxial stresses created during the forming operation can also increase the crystallization at a given temperature. U.S. Patent

No. 4,388,356 describes one method for "heat-setting" during a PET thermoforming operation (incorporated herein by reference).

A preferred method combines gas crystallization with thermoforming crystallization to create a controllable level of crystallinity in the surface layers and in the core, which may be different than that of the surface layers. For instance the surface layer can be brought up to about 14% during foaming and then subsequently raised to 29% while the interior is raised from 0% to 15% during the thermoforming operation. This combination gives independent unfoamed surface layers.

Thermoforming a polymer above a threshold crystallinity level (19% crystallinity for PET without impregnated gas) before thermoforming severely limits formability. In addition, thermoforming a polymer and then raising its crystallinity level above threshold (19% crystallinity for PET) increases the formed part's usable service temperature and strength (see, e.g., *Thermoforming, A Plastics Processing Guide*, G. Gruenwald, Technomic Publishing AG, 2d Ed.1998). It also makes the resultant part more brittle and subject to fracture at low impact.

Because of the reversible plasticizing effect of the impregnated gas described herein, crystallinity may be raised higher than the conventional process limit of 19% while still maintaining sufficient ductility for thermoforming. After thermoforming, the gas gradually migrates out of the material, being replaced by ambient gas (e.g. air), thus reversing the plasticizing effect and imparting the material qualities normally associated with the higher crystallinity. Higher temperature stability is one such material quality that may be desirable depending upon application.

This method may provide a multi-level crystalline structure that can have a very high application temperature due to its greater than threshold level surface crystallinity while at the same time have increased ductility and impact resistance due to the lower level crystallinity in the foam core and the part of the unfoamed

skin. This same principle applies to other gas- semi-crystalline polymer systems such as CO_2 -polypropylene systems.

Another aspect of this process encompasses the use of thermoforming crystallization immediately after the foaming operation as described in U.S. Patent No. 5,223,545 and before the majority of the foaming gas has been replaced by air. In a more specific embodiment illustrated in Figure 8, an impregnated roll is fed continuously through a hot-air tunnel and foamed. Thence it feeds directly into an accumulator just ahead of the thermoformer and after most of the foaming has taken place. The accumulator allows continuous movement of the roll through the foaming section while the material feed stops and starts within the thermoformer with each thermoformer cycle (lasting typically a 2 to 30 seconds.) Alternately, the roll may be stopped and started in the heating section with each thermoformer cycle thereby eliminating the accumulator.

Thermoforming within minutes or within about 24 hours after the foaming operation while the majority of foaming gas still remains in the polymer after foaming yields a number of advantages compared to the separate processes performed with hours or days between them. Increasing the time between the foaming and forming allows more and more gas to escape before thermoforming. For example, .030" thick APET saturated with 5 MPa CO_2 at room temperature retained 95% of the impregnated gas immediately after foaming. Twenty-four hours later it retained only 40% of the gas. In another example, C-PET, .028" thick saturated under the same conditions, immediately after foaming, still retained about 92% of the gas fully saturated sample. It retained only 17% of the gas of an unfoamed saturated sample after room temperature desorb of 24 hours. The gas is beneficial for thermoforming since it lowers the T_g and increases the formability of the polymer. For example, advantages of this new method include the following:

1. Saving energy and speeding up the thermoforming process by not cooling the polymer to "quench" the bubble growth as described in U.S. Patents

No. 5,684,055. Rather, immediately after most (70-98%) of the foaming has completed (typically after 30 to 75 seconds of applied foaming heat for an approximately 0.1" thick foam), the mostly foamed sheet is fed into a thermoformer and heating is continued to a typical thermoforming temperature significantly above the T_g for a few seconds. This saves energy and speeds up the combined process since the time required for cooling and a later reheating in the thermoformer is eliminated. If most of the foaming were to take place in the thermoformer, the cycle rate of the thermoformer and production rate would be greatly slowed due to the required foaming time of 30 or more seconds (2 cpm). Thus by allowing most or essentially all of the foaming to take place in a heating system separate from the thermoformer, the thermoformer cycle rate is greatly increased (30 cpm is typical). Thus a higher article production rate is obtainable by creating most of the foam prior to the thermoforming operation.

2. Improved part detail due to the combined thermoforming-foaming operation. This combined operation allows a small percentage of the foaming (2% to 30%) to take place during contact with the thermoforming die which will create better detail by filling in the die details.

3. Shortening the cycle time and saving energy to reach a given level of crystallization after thermoforming by allowing a higher percentage of polymer crystallization going into the thermoformer. If a significant time is allowed to pass (more than a day) before thermoforming the foam strip or sheet into a product then significant amounts of CO_2 gas will have left the foam. By thermoforming within minutes or hours after foaming, the remainder CO_2 acts as a lubricant between polymer chains and increases the formability of the polymer so a higher percentage of crystallinity is allowed going into the thermoformer without cracking problems during the forming operation. The holding time in the thermoformer to reach a given finished crystallinity level is reduced by being able to start at a higher crystallinity level without part cracking during thermoforming.

4. Shortening the cycle time and saving energy to reach a given level of crystallization after thermoforming. If a significant time is allowed to pass (more than many minutes) before thermoforming the foam strip or sheet into a product then significant amounts of CO_2 gas will have left the foam. By thermoforming within minutes after foaming, the remainder CO_2 acts as a lubricant between polymer chains and increases the propensity of the polymer toward forming crystalline structures during the heating and forming operations. The holding time in the thermoformer to reach a given finished crystallinity level is thus reduced.

5. The plastics lower strength due to the impregnated gas, improves the die trim operation reducing the need for added trim or trim-die heat.

6. It allows optimization of crystallinity levels in a bi-crystallinity level structure in foamed and thermoformed parts. The levels are optimized so that (a) the surface crystallinity level is above a threshold level that significantly raises the part's strength and useable service temperature, and (b) the core's crystallinity level is just below a threshold level where brittleness sharply increases. The foam core after thermoforming includes a significant central layer of low crystallinity level material with high impact properties compared to the highly crystallized outer layers. The resultant parts will have increased ductility and impact resistance due to the flexible core for a given allowable service temperature.

Further distinguishing characteristics of this invention, particularly when compared to the product of U.S. Patent No. 5,182,307, include the following:

1. The thickness of the unfoamed skin is independent of the depth from the surface of high crystallinity level material as illustrated in Fig 12

2. The crystallinity level of the core layer after thermoforming is not that of the unfoamed material, but is significantly higher while still much lower than the high level surface material.

3. The low-crystallinity core layer thickness is independent of the thickness of foamed center material.

4. The material may be any semicrystalline polymer foamed with a gas that acts as a solvent for the polymer and lower the glass-transition temperature (T_g) of the polymer such as polypropylene with CO_2 gas or PET with CO_2 gas or Polystyrenc with N_2.

In another embodiment, gas impregnated sheet or roll stock of amorphous polymer (for example, polyvinyl chloridc and polycarbonate) is saturated without regard to crystallinity levels as described above using the "semi-continuous process." It is then thermofonned shortly thereafter without significant foaming taking place in the thermoformer. In this embodiment, the gas simply serves as a plasticizer and not as a crystallizing agent. With this embodiment, thermoforming must take place while significant gas remains in the polymer. For a previously foamed material, the desorb time before thermoforming must be a few minutes to about a day to retain significant gas. In this embodiment, accrued advantages include increased formability during thermoforming or lower temperature thermoforming for a given draw ratio, shorter cycle time, reduced energy consumption, and improved die trimming.

In another embodiment, gas impregnated sheet or roll stock of previously foamed polymer (whether foamed with the semi-continuous process or any other means), is saturated with plasticizing and/or crystallizing gas. without significant foaming taking place in the thermoformer. In this embodiment, the gas may simply serve as a plasticizer and not as a crystallizing agent.

All of the above U.S. patents, U.S. patent application publications, U.S. patent applications, foreign patents, forcign patent applications and non-patent publications referred to in this specification and/or listed in the Application Data Sheet, are incorporated herein by reference, in their entirety.

The preceding overview of the invention, brief description of the drawings, and detailed description dcscribe exemplary embodiments of the present invention in a manner intended to foster ease of understanding by the reader. Other structures, methods, and equivalents may be within the scope of the invention. As

such, the scope of the invention described herein shall be limited only by the claims.

CLAIMS

Insert claims at conversion to regular application.

Some possible claims:

A method for making a thermoformed foamed article, comprising the three steps of: (1) Impregnating a thermoplastic material with a plasticizing gas to form an impregnated thermoplastic material containing at least .5% by weight plasticizing gas; (2) Foaming the impregnated thermoplastic material to form a foamed thermoplastic material containing at least 0.45% by weight plasticizing gas; and (3) Thermoforming the foamed thermoplastic material while containing at least 0.45% by weight plasticizing gas to yield the thermoformed article.

2. A method for making a thermoformed article, comprising the 2 steps of:

(1) Impregnating a thermoplastic material with a plasticizing gas to form an impregnated thermoplastic material containing at least 0.5% by weight plasticizing gas; (2) thermoforming the gas-impregnated thermoplastic material containing at least 0.5% by weight of a plasticizing gas under conditions such that the thermoplastic materials does not foam during the step of thermoforming.

- Wherein the gas-impregnated thermoplastic material has a previously foamed or cellular structure

- wherein the gas impregnated thermoplastic material is a solid (non-foamed) thermo material (discuss added benefits)

1. A thermoformed article, comprising a foamed core and a crystalline surface layer, and a non-foamed layer disposed between the foamed core and the crystalline surface layer.

1. A method for control of the relative crystallinity levels in the surface layers independently of the crystallinity level in the inner core when manufacturing thermoformed PET foam articles consisting of: (1)The "semi-continuous" process (US Patent No. 5,684,055) with saturation times (for instance, less than 190 hours at room temperature) in the pressure vessel insufficient to limit crystallinity levels before foaming below a threshold (19% for PET) that restricts foaming later in the process. After foaming, the thickness of the unfoamed skin may be thicker or thinner than the high crystallinity layer thickness.

2. A method for control of the relative crystallinity levels in the surface layers as well as in the inner core of any semi-crystalline polymer (including but not limited to such as polypropylene, polyethylene, Nylon 6, or PET) when manufacturing thermoformed foam articles as described in claim 1

3. A method for decreasing the cycle time and saving energy when manufacturing thermoformed foam articles of any thermoplastic polymer using the "semi-continuous" process (US Patent No. 5,684,055) as the foaming method, by immediately following the foaming process with a thermoforming process. This allows the retained foaming gas to increase the formability during the forming operation allowing shorter heating times and lower forming temperatures.

4. A method as described in claim 3 for increasing the formability of foamed polymers allowing deeper draws when manufacturing thermoformed foam articles.

5. A method as described in claim 3 for increasing the formability of foamed polymers allowing higher crystallinity levels for a given draw ratio during the thermoforming operation while manufacturing thermoformed foam articles.

6. A method as described in claim 5 for saving energy when manufacturing thermoformed foam articles. The higher crystallinity level entering the thermoformer reduces the heating required during thermoforming to reach a given finished crystallinity level.

7. A method as described in claim 3 for improving the surface detail when manufacturing thermoformed foam articles allowing a small percentage of the foaming to take place in contact with a thermoformer die.

8. A method for producing a bi-level crystallinity structure in foamed and thermoformed semi-crystalline polymer parts that can both:

1. Have a high part-application temperature due to a surface crystallinity level above a threshold level that significantly raises the part's strength and useable service temperature.
2. Have increased ductility and impact resistance due to a crystallinity level in the foam core just below a threshold level where brittleness sharply increases.

9. A method for producing a bi-level crystallinity structure in foamed and thermoformed PET polymer parts that can both:

1. Have a high part-application temperature due to a surface crystallinity level significantly above a threshold level (approximately 19%) that significantly raises the part's strength and useable service temperature.
2. Have increased ductility and impact resistance due to a reduced crystallinity level in the foam core.

11. A semicrystalline foamed polymer with a layered structure having crystallinity levels in the surface layers higher than those in the inner layer. The foamed inner core thickness is different than the thickness of the low crystallinity layer. These polymers may include polypropylene, polyethylene, Nylon 6, and Polyethylene Terephthalate (PET)

12. A bi-level crystallinity structure in foamed and thermoformed polymer parts that can both:

1. Have a high part-application temperature due to a surface crystallinity level above a threshold level that significantly raises the part's strength and useable service temperature.
2. Have increased ductility and impact resistance due to a crystallinity level in the foam core just below a threshold level where brittleness sharply increases.

13. A bi-level crystallinity structure in foamed and thermoformed PET polymer parts that can both:

1. Have a high part-application temperature due to a high surface crystallinity level (for instance 30%) significantly above a threshold level (approximately 19%) that significantly raises the part's strength and useable service temperature.
2. Have increased ductility and impact resistance due to a crystallinity level in the foam core just below the 19% threshold level where brittleness sharply increases.

14. A foamed polymer with surfaces of unfoamed skin thicker than the high crystallinity level layer in a bi-level crystallinity structure described in claim 12

15. A foamed polymer with surfaces of unfoamed skin thinner than the high crystallinity level layer in a bi-level crystallinity structure described in claim 12.

16. A foamed PET polymer with surfaces of unfoamed skin thicker than the more than 19% crystallinity level layer in a bi-level crystallinity structure described in claim 12.

17. A foamed PET polymer with surfaces of unfoamed skin thinner than the high crystallinity level layer in a bi-level crystallinity structure described in claim 12 where the high crystallinity layer has less than 19% crystallinity.

18. A method for decreasing the thermoforming cycle time when manufacturing thermoformed foam articles of any thermoplastic polymer using the "semi-continuous" process (US Patent No. 5,684,055) as the foaming method by immediately following the foaming process with the thermoforming process.

19. A method for saving energy when manufacturing thermoformed foam articles of any thermoplastic polymer using the "semi-continuous" process (US Patent No. 5,684,055) as the foaming method by immediately following the foaming process with the thermoforming process. This allows the foaming gas to increase the formability during the forming operation allowing lower forming temperature for a given draw ratio. The foaming temperature is approximately the polymer's Tg. The thermoforming temperature is significantly above the Tg (on the order of 20-100 degrees C or more above the Tg.

20. A method as described in claim 19 for increasing the formability of foamed polymers allowing deeper draws when manufacturing thermoformed foam articles.

21. A method as described in claim 19 for reducing the polymer heat-degradation when manufacturing thermoformed foam articles.

22. A method as described in claim 19 for improving the surface detail when manufacturing thermoformed foam articles allowing a small percentage of the foaming to take place in contact with a thermoformer die.

SHEET 1/6

Fig. 1

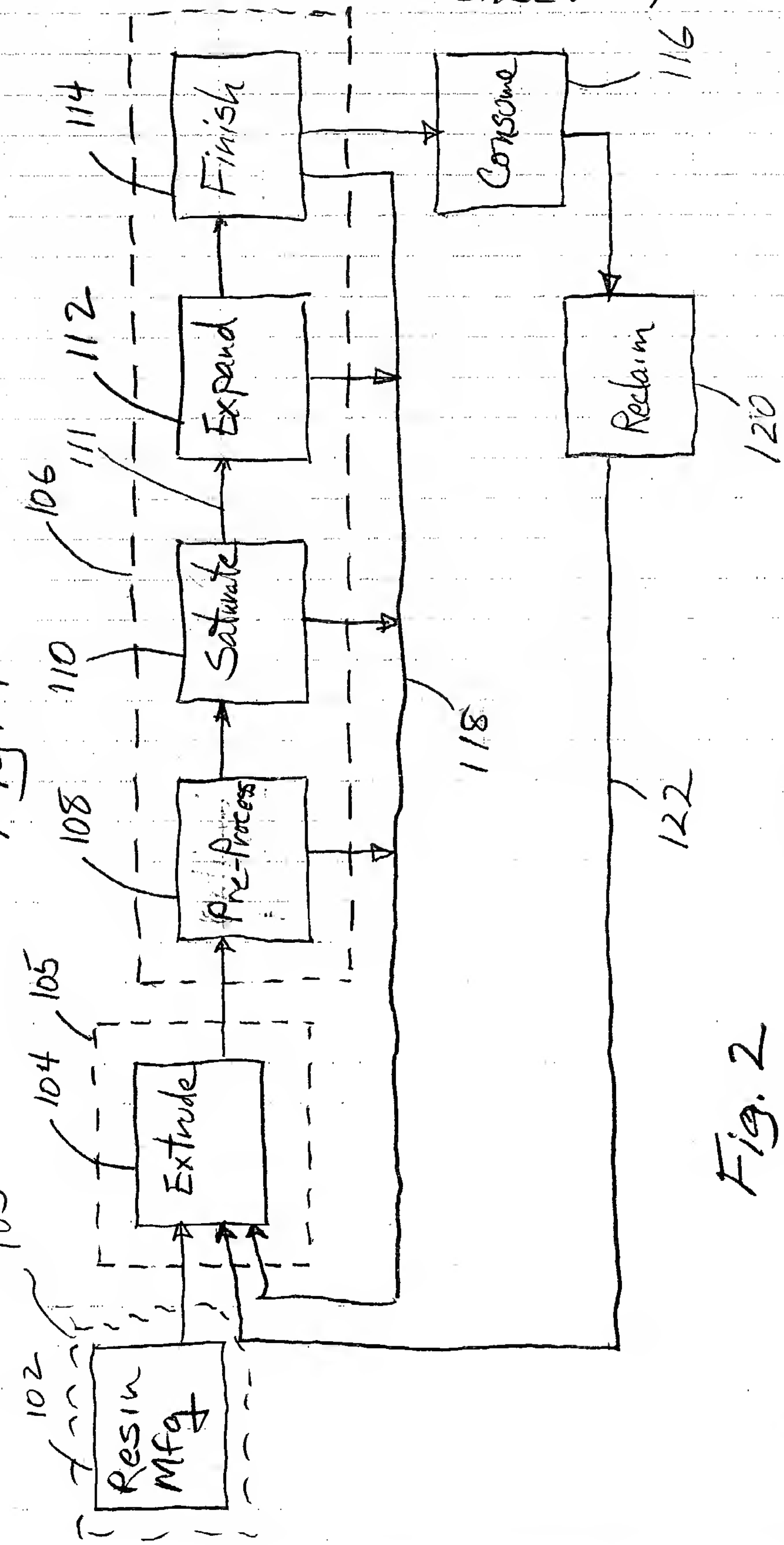
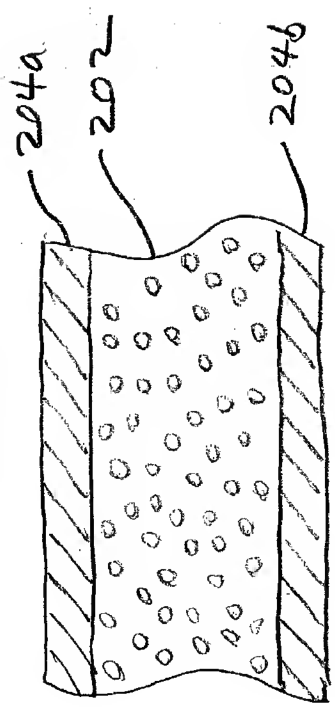


Fig. 2



SHEET 2/6

Fig. 3

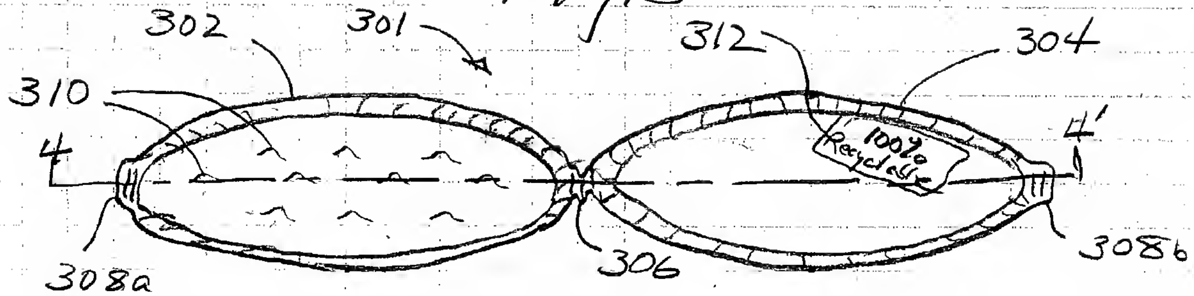


Fig. 4

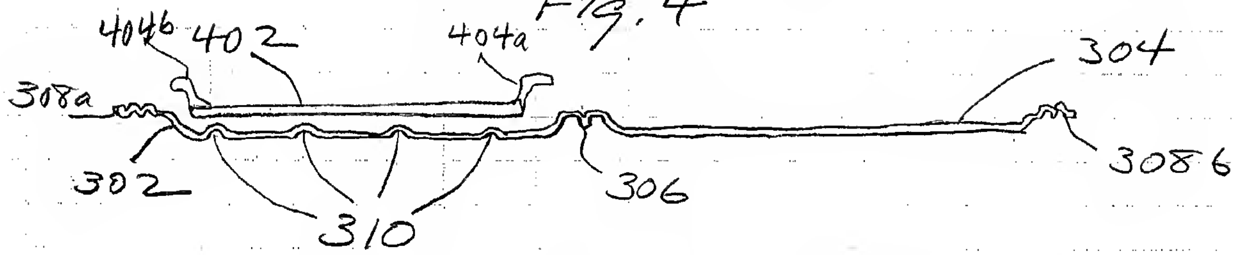


Fig 5

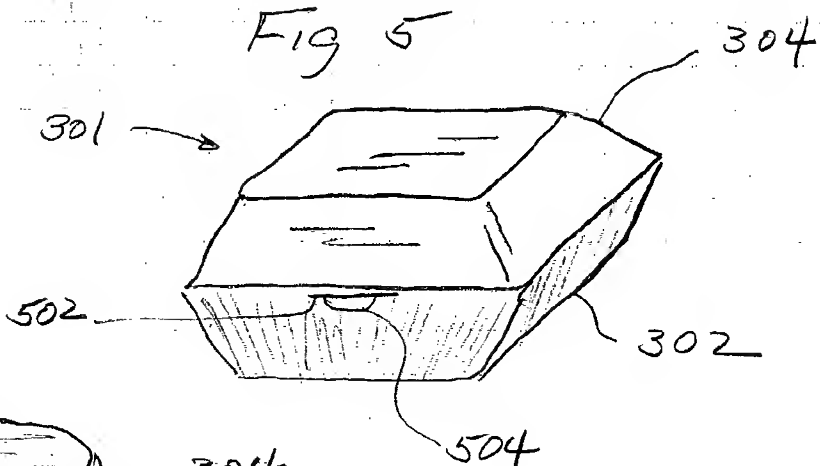


Fig 6

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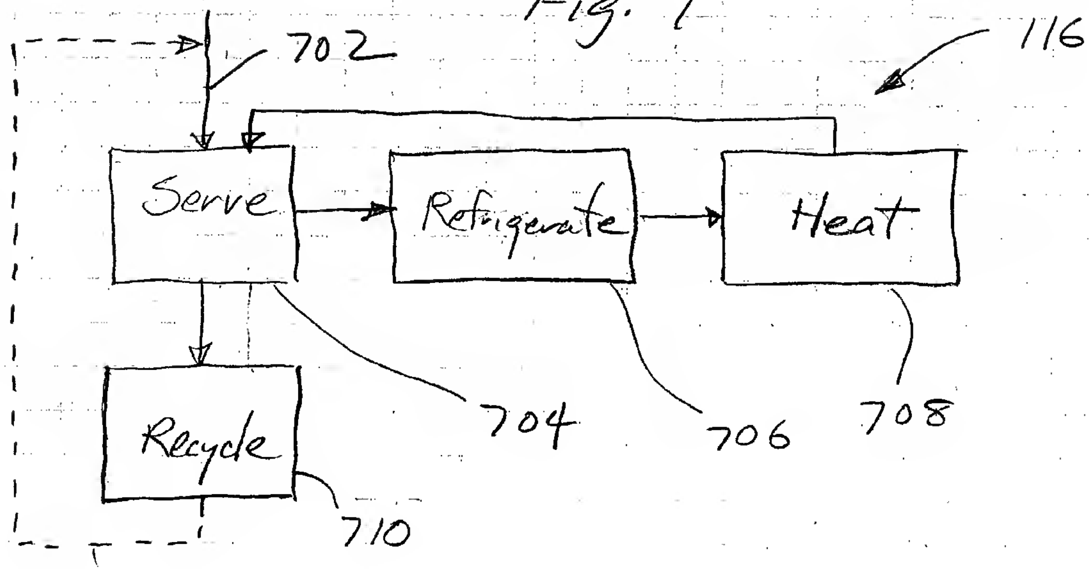
Fig. 7



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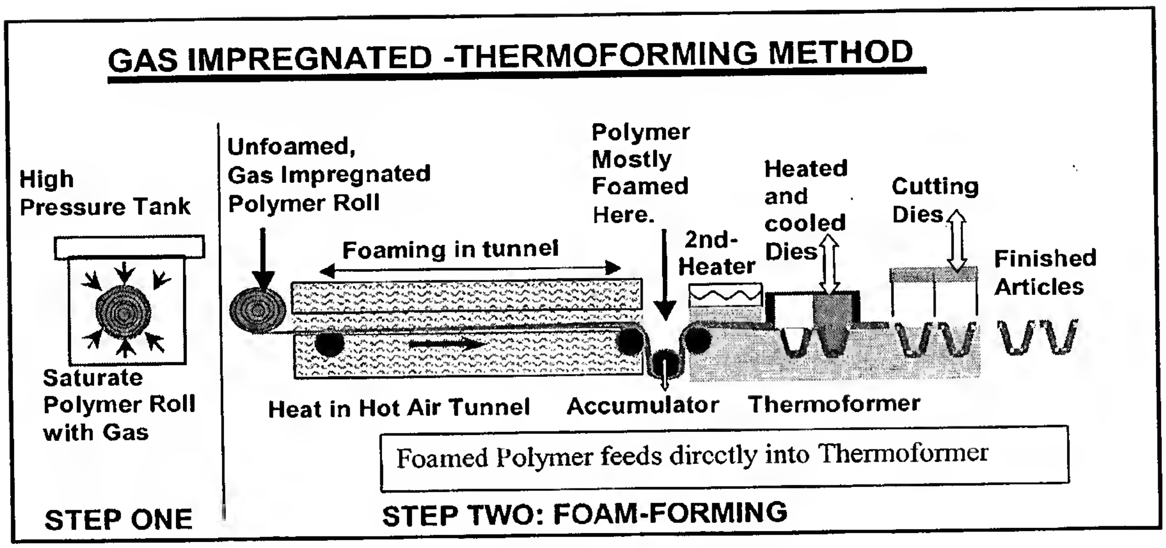
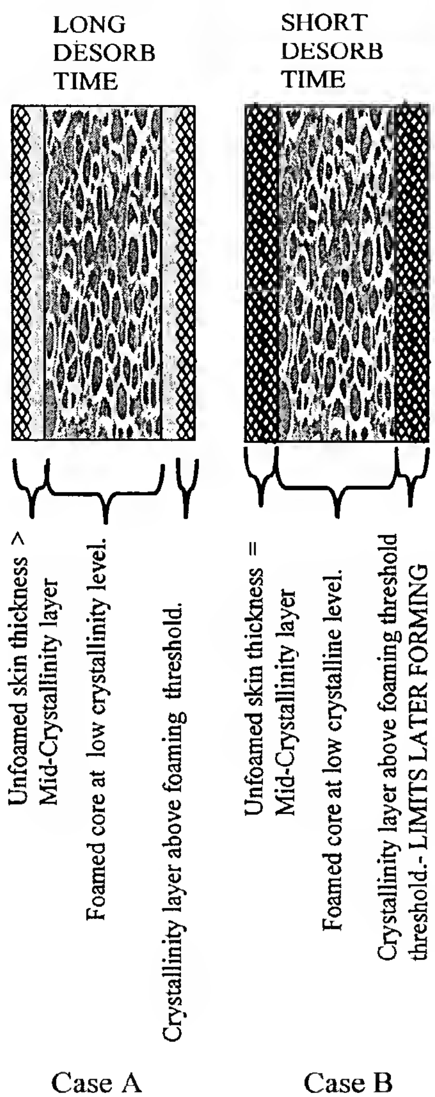


Figure ~~1~~ 8

SHEET 5/6

Polymer Cross Sections With First-Step Crystallinity Level Above The Threshold That Limits Foaming and Formability

AFTER FOAMING and BEFORE THERMOFORMING



ALL CRYSTALLINITY INCREASED AFTER THERMOFORMING

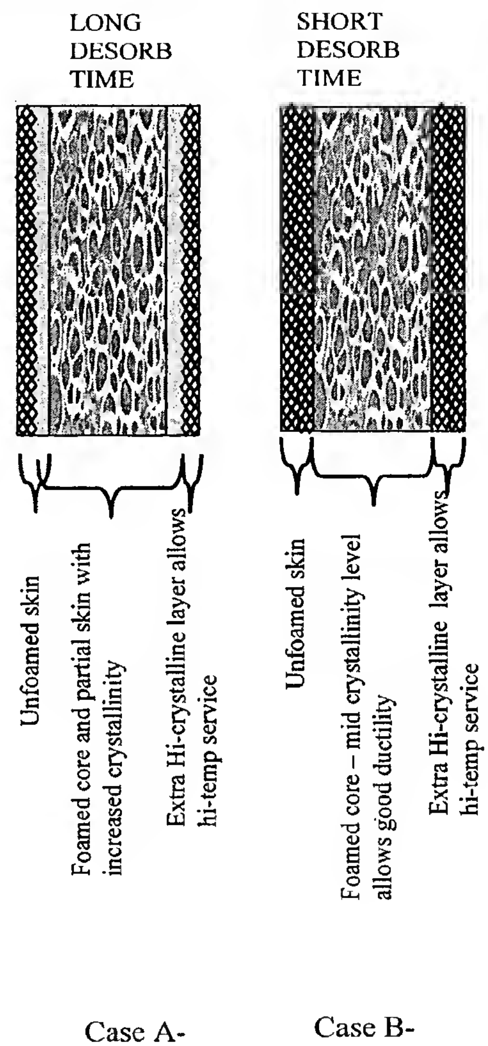


Figure ~~2~~ 9

Figure ~~3~~ 10

SHEET 6/6

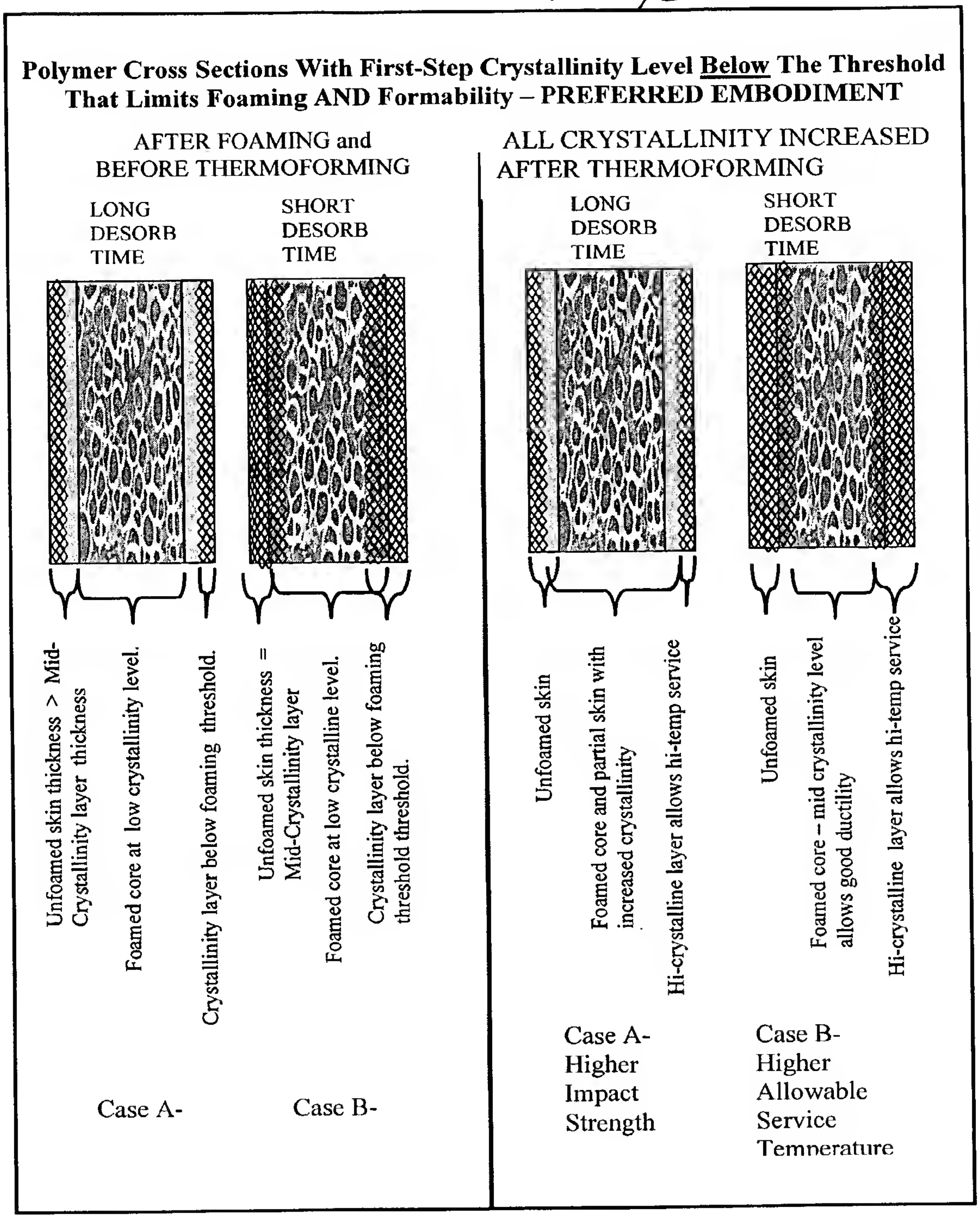


Figure ~~4~~ 11

Figure ~~5~~ 12